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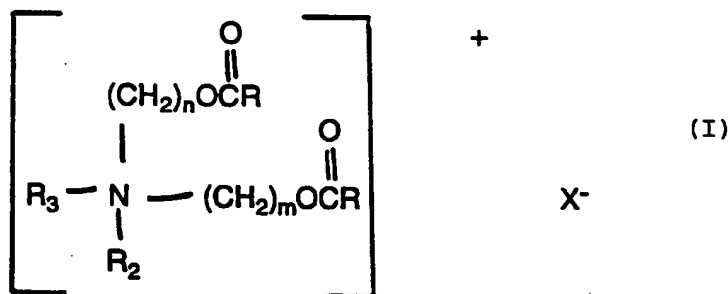
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<p>(21) International Application Number: PCT/US93/07607 (22) International Filing Date: 17 August 1993 (17.08.93) (30) Priority data: 07/934,100 21 August 1992 (21.08.92) US 08/086,809 2 July 1993 (02.07.93) US (71) Applicant: COLGATE-PALMOLIVE COMPANY [US/ US]; 300 Park Avenue, New York, NY 10022 (US). (72) Inventors: GRANDMAIRE, Jean-Paul ; Rue Sous le Châ- teau 45, B-4821 Andrimont (BE). TACK, Viviane ; Rue Baudrihay 17, B-4630 Soumagne (BE). JACQUES, Alain ; Rue de l'Institut 202, B-4570 Blegny (BE). HAR- MALKER, Subhash ; 11 Gifford Road, Somerset, NJ 08873 (US).</p>		<p>(74) Agent: LIEBERMAN, Bernard ; Colgate-Palmolive Com- pany, 909 River Road, Piscataway, NJ 08855-1343 (US). (81) Designated States: HU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: RINSE CYCLE FABRIC SOFTENER



(57) Abstract

An environmentally compatible and biodegradable rinse cycle fabric conditioning composition is provided capable of providing improved softening with significant reduction and solubilization of unwanted mineral encrustations on fabrics to be softened. The composition comprises: (a) from about 1 to about 20 %, by weight, of a diesterified long chain fatty acid cationic fabric softener represented by general formula (I), wherein RCO represents the residue of a fatty acid having from about 12 to 24 carbon atoms; R₂ and R₃ represent independently a lower alkyl group or a hydroxyalkyl group having 1 to 4 carbon atoms; n and m are integers from 1 to 4 and X is a water-solubilizing anion; and (b) from about 1 to about 25 %, by weight, of unreacted organic or mineral acid.

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RINSE CYCLE FABRIC SOFTENER

BACKGROUND OF THE INVENTION

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This invention relates to fabric softening compositions which are suitable for softening in the rinse cycle of an automatic household washing machine, and which are especially adapted for use under European laundering conditions. More particularly, the present invention relates to fabric conditioning compositions comprising a diesterified quaternary ammonium salt in combination with an acid and optionally a fatty alcohol, which compositions are characterized by superior environmental compatibility relative to conventional quaternary ammonium fabric softening compositions concomitant with providing improved calcium salt solubilization and reduction of encrustation on treated fabrics.

Esterified quaternary ammonium salts are known in the art as fabric softeners, and are generally recommended for use in combination with fatty alcohols or linear alkoxyolated alcohols. U.S. Patent 4,844,823 to Jacques et al describes a diesterified long chain fatty acid di lower-alkyl quaternary ammonium salt as a preferred class of cationic fabric softeners for use in conjunction with a fatty alcohol having from 10 to 24 carbon atoms. In EP-A-309,052 there is disclosed a liquid softening composition containing a monoester or diester quaternary ammonium compound in combination with an alkoxyolated alcohol which is said to reduce the ester hydrolysis rate of the quaternized softening compound, thereby improving its chemical stability.

The combination of organic acid with cationic fabric softener is also disclosed in the prior art. U.S. Patent 3,904,359 and 3,954,630 to Ramachandran disclose a fabric treating composition comprising a complexing acid such as citric or maleic acid in combination with a quaternary ammonium softening compound. The function of the acid, as stated in the patent, is to prevent yellowing of fabrics due to build-up of cationic softener and to provide a complexing site for metal ions contained in soils. U.S. Patent 4,162,984 describes a mixture of a quaternary ammonium salt and an aromatic carboxylic acid such as benzoic acid to provide an emulsion having significantly increased viscosity. U.S. Patent 4,426,299 discloses a fabric softening composition comprising a defined quaternary ammonium compound and a viscosity control agent which may be a C₉-C₂₄ fatty acid. In U.S. Patent 4,559,151 there is disclosed the combination of quaternary ammonium salts with a lactic acid salt for the purpose of imparting improved antistatic properties. U.S. Patent 4,832,856 discloses mixtures of carboxylic acids with defined amines and/or quaternary ammonium

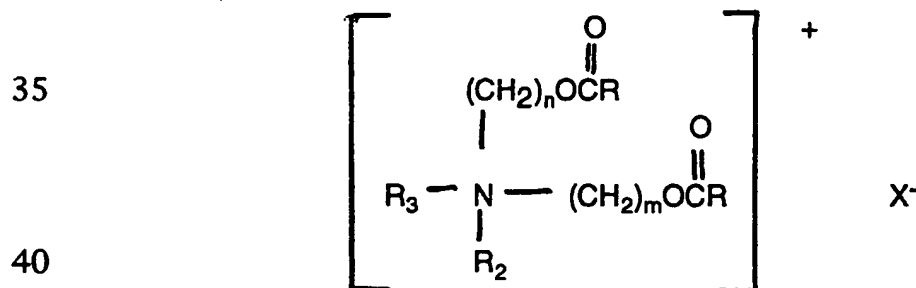
compounds, the resulting mixture being said to provide softening using inexpensive raw materials. EP 404,471 relates to an isotropic liquid fabric softener comprising at least 20% of a fabric softening material and at least 5% of an organic acid, the isotropic compositions being said to be more stable than lamellar structures. DE 3,312,328 (Benkiser) similarly describes a composition containing a fabric softener material and an organic acid. The addition of acid serves to complex alkaline earth and heavy metal ions.

Although satisfactory results may be obtained with one or more of these prior art fabric softening compositions, further improvements are needed in terms of being able to provide efficacious fabric softening with a biodegradable cationic fabric softening compound, concomitant with the ability to substantially solubilize and remove mineral encrustation from the fabrics to be treated. This is a particularly important need for European fabric conditioning compositions where the cumulative deposition of mineral salts on fabrics during repetitive laundering in hard water is an acute problem. Moreover, the increased emphasis in Europe on using biodegradable softening compounds which have no toxic effect on aquatic organisms in aqueous effluent streams makes it imperative that conventional softening compounds, notably, the di-long chain, di-short chain quaternary ammonium compounds be replaced as the softening compounds of choice in commercial rinse-cycle softening compositions with softening compounds which are significantly more compatible with environmental concerns.

SUMMARY OF THE INVENTION

The present invention provides environmentally compatible and biodegradable rinse cycle fabric conditioning compositions capable of providing improved softening with significant reduction and solubilization of unwanted mineral encrustations on fabrics to be softened, such encrustations having been generally deposited on the fabrics during the course of prior laundering in water having a high mineral content, which comprises:

(a) from about 1 to about 20%, by weight, of a diesterified long chain fatty acid cationic fabric softener represented by the general formula



wherein RCO represents the residue of a fatty acid having from about 12 to 24 carbon atoms;

R₂ and R₃ represent independently a lower alkyl group or a hydroxyalkyl group having 1 to 4 carbon atoms;

5 n and m are integers from 1 to 4 and X is a water-solubilizing anion; and
(b) from about 1 to about 25%, by weight, of unreacted organic or mineral acid.

10 In a preferred embodiment of the invention, the fabric softening composition further contains from about 0.2 to about 5%, by weight, preferably from about 0.5 to about 3%, and most preferably from about 0.5 to 1%, by weight, of a fatty alcohol having from about 10 to about 24 carbon atoms.

15 In another preferred embodiment of the invention the cationic fabric softener is a triethanolamine diester which comprises N-methyl, N, N-di (beta C₁₄-C₁₈ acyloxy-ethyl), N-beta hydroxy ethyl ammonium, and the anion is halide, methylsulfate or ethylsulfate.

The invention also encompasses a method for softening fabrics and removing unwanted mineral encrustations therefrom comprising rinsing the fabrics to be treated in an aqueous bath containing an effective amount of a composition comprised of the above-defined fabric softening composition.

20 The present invention is predicated on the discovery that the combination of cationic fabric softener as defined above with an organic or mineral acid provides a biodegradable softener which has the capability of removing mineral encrustations such as calcium and magnesium salts, and in particular, phosphates and carbonates of calcium and magnesium, which cumulatively deposit on the fabrics during the
25 course of prior laundering in hard water, i.e. water having a mineral content above about 300 ppm, conditions generally associated with European laundering conditions.

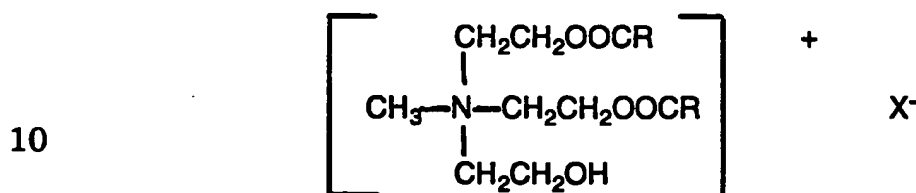
30 A particularly preferred softening compound as described herein comprises di(stearoyl-oxyethyl-) methyl-hydroxyethyl ammonium, and X is a halide, methosulfate or ethylsulfate.

DETAILED DESCRIPTION OF THE INVENTION

35 The compositions of the present invention are environmentally compatible and biodegradable rinse cycle fabric conditioning compositions which contain as the active fabric softening compound a diesterified long chain fatty acid cationic fabric softener as defined above. The use of such fabric softening compound avoids the more traditional di-long chain, di-short chain quaternary ammonium softeners which are used extensively in commercial rinse cycle softeners, but which presently have

become the focus of increasing legislative concerns, particularly in Europe, because of their lack of biodegradability in aqueous effluent streams.

A preferred "diesterified quat" in accordance with the invention is commercially available from, for instance, Stepan Chemical Co. under the Stepanex trademark,
 5 such as Stepanex VHR90 which has the formula



where R is hydrogenated or non-hydrogenated tallow and X may be chloride or sulfate.

15 The total amount of diesterified cationic fabric softener in the total composition is from about 1 to 20%, by weight, preferably from about 2 to 10%, by weight.

The second essential ingredient of the fabric conditioning composition is the acid which has a dual function, depending on the acid concentration. The first function is preventive in nature and occurs when the acid in the diluted rinse cycle solution is
 20 present in sufficient amount to react with the insoluble salts of the water hardness ions (calcium and magnesium) to form soluble acid salts and to remove any mineral salts which may have deposited on fabrics during the washing step of the wash cycle. The second function is more curative in nature and refers to the removal of mineral encrustations which have been cumulatively deposited during prior washing
 25 throughout the fabric's life.

To effect the aforementioned preventive function, an acid concentration of from about 1 to about 8%, by weight, preferably from about 5 to about 8%, is required in the fabric softening composition depending on the dosage used and the hardness of the water. For European washing machines containing about 20 to 25 liters of water, for
 30 example, a dosage of 110 to 150 ml of softening composition is typical for use in the rinse cycle; the water hardness varies from about 200 to 400 ppm, most typically about 300 ppm. To effect the curative function of the acid for removal of previously deposited mineral encrustations, an acid concentration of from about 5 to about 25%, by weight, preferably from about 8 to 25%, by weight, is required in the fabric softening
 35 composition.

The acid used may be an organic or mineral acid. The organic acids are preferably saturated or unsaturated C₂-C₆ carboxylic acids such as citric acid, formic acid, maleic acid, tartaric acid and succinic acid. Citric acid, malonic acid and maleic acid are particularly preferred. A mineral acid, such as HCl, may be used

advantageously in combination with such organic acid, the amount of acid used in excess of protonation being referred to herein as "excess".

5 An optional fabric conditioning ingredient is a fatty alcohol wherein the hydrophobic group may be a straight or branched chain alkyl or alkenyl group having from about 10 to 24, preferably from about 10 to 20, especially preferably from about 12 to 20 carbon atoms. Specific examples of the fatty alcohol include decanol, dodecanol, tetradecanol, pentadecanol, hexadecanol, octadecanol, lauryl alcohol, palmityl alcohol, stearyl alcohol, oleyl alcohol, and mixtures thereof. Furthermore, the fatty alcohol may be of natural or synthetic origin and may include, for example, mixed
10 alcohol, such as C₁₆-C₁₈ alcohols prepared by Ziegler polymerization of ethylene.

The fatty alcohol may be present in the composition in a minor amount relative to the cationic fabric softener such that the ratio, by weight, of the cationic fabric softener to fatty alcohol is in the range of from about 6:1 to 2:1, preferably about 5:1 to 3:1, and most preferably about 4:1.

EXAMPLE 1

Compositions A and B in accordance with the invention were prepared as described below, and compared to the Reference Composition which is in accordance with the prior art.

5

	<u>Composition A</u>	<u>Weight %</u>
10	N, N-Di(stearoyl-oxyethyl) ester, N-methyl, N-ethanol ammonium chloride	5.5
	Synperonic A 20 ⁽¹⁾ (emulsifier)	0.3
	Citric Acid	10.0
15	Perfume	0.3
	Preservative and colorant	less than 0.1
20	Water	balance

25

(1) A nonionic surfactant comprised of
C₁₃₋₁₅ alcohol ethoxylate having 20 moles
EO/mole alcohol.

30

	<u>Composition B</u>	<u>Weight %</u>
30	N, N-Di(stearoyl-oxyethyl) ester, N-methyl, N-ethanol ammonium chloride	3.3
	Fatty alcohol (C ₁₆₋₁₈ alcohol)	0.83
35	Synperonic A 20 (emulsifier)	0.3
	Citric acid	10.0
	Perfume	0.3
40	Preservative and colorant	less than 0.1
	Water	Balance

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	<u>Reference Composition</u>	<u>Weight %</u>
5	Ditallow dimethyl ammonium chloride	5.0
	Perfume	0.3
	Preservative and colorant	less than 0.1
10	Sodium chloride	less than 0.1
	Water	Balance

15 Each of softening compositions A, B and the Reference Composition were added to the rinse cycle of a European washing machine having 25 liters of water in a dosage of 4.4 grams per liter of water and containing previously encrusted towels containing 24%, by weight, encrustation. The softening performance of each composition was evaluated by a three member panel. All three softening compositions were graded by the panel as providing the same softening performance.

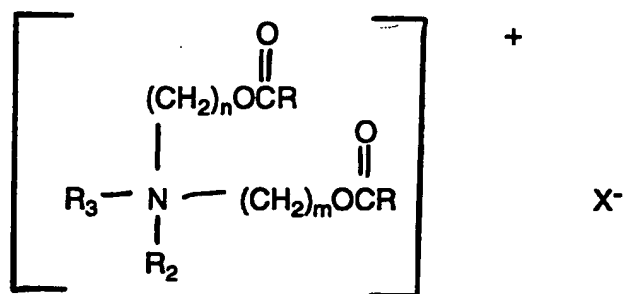
20 The percent of encrustation solubilization on the encrusted fabrics was measured for all three of the tested compositions. The encrustation level was measured by calcination of the encrusted fabrics whereby weight measurements were taken before and after calcination of the fabric in an oven at 800°C for 1 hour. After calcination, the organic materials such as the fibers and detergents are burned in the
25 oven with only the minerals remaining; the latter being primarily calcium phosphate salts, i.e. encrustations.

The encrustation solubilization, expressed as a percentage, refers to the amount of encrustation removed during the rinse cycle treatment relative to the amount of encrustation present originally. For Compositions A and B the percent of
30 encrustation solubilization was 2.3%; for the Reference composition, less than 0.1% of encrustation was solubilized.

CLAIMS

1. An environmentally compatible and biodegradable rinse cycle fabric conditioning composition capable of providing improved softening with significant reduction and solubilization of unwanted mineral encrustations on fabrics to be softened, such encrustations having been generally deposited on the fabrics during the course of prior laundering in water having a high mineral content, which comprises:

(a) from about 1 to about 20%, by weight, of a diesterified long chain fatty acid cationic fabric softener represented by the general formula



wherein RCO represents the residue of a fatty acid having from about 12 to 24 carbon atoms;

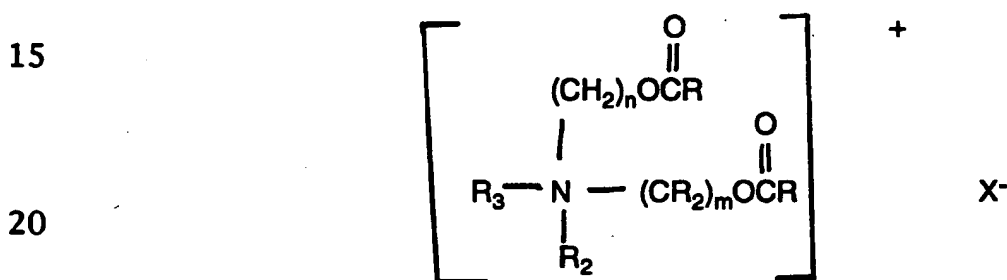
R₂ and R₃ represent independently a lower alkyl group or a hydroxyalkyl group having 1 to 4 carbon atoms;

n and m are integers from 1 to 4 and X is a water-solubilizing anion; and

(b) from about 1 to about 25%, by weight, of unreacted organic or mineral acid.

2. A fabric conditioning composition according to claim 1 wherein said cationic fabric softener is a triethanolamine diester which comprises N-methyl, N, N-di (beta C₁₄-C₁₈ acyloxy-ethyl), N-beta hydroxy ethyl ammonium, and wherein X is a halide, methylsulfate, or ethylsulfate.
3. A fabric conditioning composition according to claim 1 wherein said cationic fabric softener comprises di (stearoyl-oxyethyl) methyl-hydroxyethyl ammonium and X is a halide, methylsulfate or ethylsulfate.
4. A fabric conditioning composition according to claim 1 which further includes from about 0.2 to about 5%, by weight, of a fatty alcohol having from about 10 to about 24 carbon atoms.
5. A fabric conditioning composition according to claim 1 wherein the concentration of acid is from about 8 to 25%, by weight, of the fabric conditioning composition.

6. A fabric conditioning composition according to claim 1 wherein the acid is citric acid.
7. A fabric condition composition according to claim 1 wherein the acid is malonic or maleic acid.
- 5 8. A fabric conditioning composition according to claim 4 wherein the fatty alcohol is a C₁₆-C₁₈ alcohol.
9. A method for softening fabrics and removing unwanted mineral encrustation therefrom comprising rinsing the fabrics to be treated in an aqueous bath containing an effective amount of a rinse cycle fabric conditioning composition comprising
- 10 (a) from about 1 to about 20%, by weight, of a diesterified long chain fatty acid cationic fabric softener represented by the general formula



- wherein RCO represents the residue of a fatty acid having from about 12 to 24 carbon atoms;
- 25 R₂ and R₃ represent independently a lower alkyl group or a hydroxyalkyl group having 1 to 4 carbon atoms;
- n and m are integers from 1 to 4 and X is a water-solubilizing anion; and
- (b) from about 1 to about 25%, by weight, of unreacted organic or mineral acid.
- 30 10. The method of claim 9 wherein said cationic fabric softener comprises N-methyl, N, N-di(beta C₁₄C₁₈ acyloxy-ethyl), N-beta hydroxy ethyl ammonium, and wherein X is a halide, methylsulfate, or ethylsulfate.
11. The method of claim 9 wherein the concentration of acid is from about 8 to 25%, by weight, of the fabric conditioning composition.
- 35 12. The method of claim 9 wherein the acid is citric acid.
13. The method of claim 9 wherein the acid is malonic acid or maleic acid.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/07607

A. CLASSIFICATION OF SUBJECT MATTER IPC 5 C11D1/62 C11D3/02 C11D3/20		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 5 C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	EP,A,0 345 495 (HENKEL KGAA.) 13 December 1989 see page 2, line 39 - line 54; claims 1-7; examples 3-5 ---	1,6,9,12
A	EP,A,0 423 894 (COLGATE - PALMOLIVE CO.) 24 April 1991 see the whole document ---	1
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
9 February 1994		15.02.94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Serbetsoglou, A

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